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(54) **METHODS AND SYSTEMS FOR CHARGING  
ELECTROCHEMICAL CELLS**

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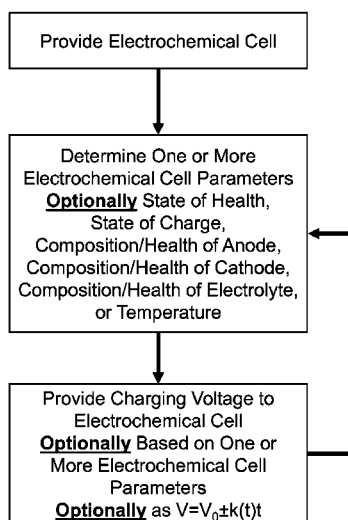
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**ABSTRACT**

The invention provides systems and methods for charging an electrochemical device, such as a secondary electrochemical cell. Charging systems and methods of some embodiments provide charging parameters, such as charging voltage and charging current, that vary in a preselected manner as a function of time so as to enhance the overall device performance (e.g., specific capacity, discharge rate, etc.) cycling properties and useful lifetime of a secondary electrochemical cell. Charging systems and methods of some embodiments provide charging parameters, such as time varying charging voltages and charging currents, that take into consideration important electrochemical cell properties that impact device performance, cycling and lifetime, such as the state of health of an electrochemical cell, and/or the health and/or composition of specific system components such as anode, cathode, and electrolyte and/or the cycle history of the electrochemical cell (e.g., cycle number, etc.).

**31 Claims, 2 Drawing Sheets**



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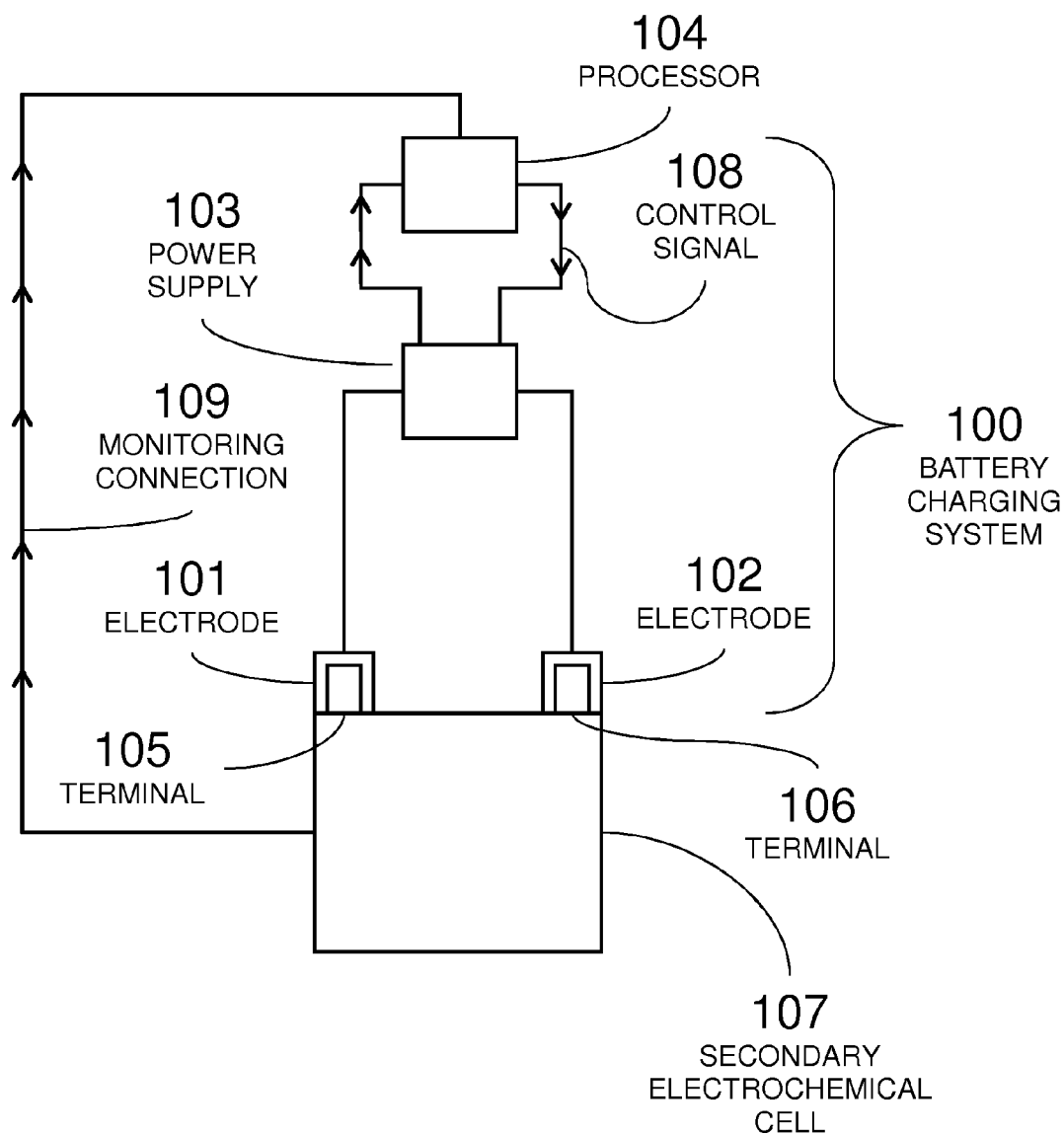


Figure 1

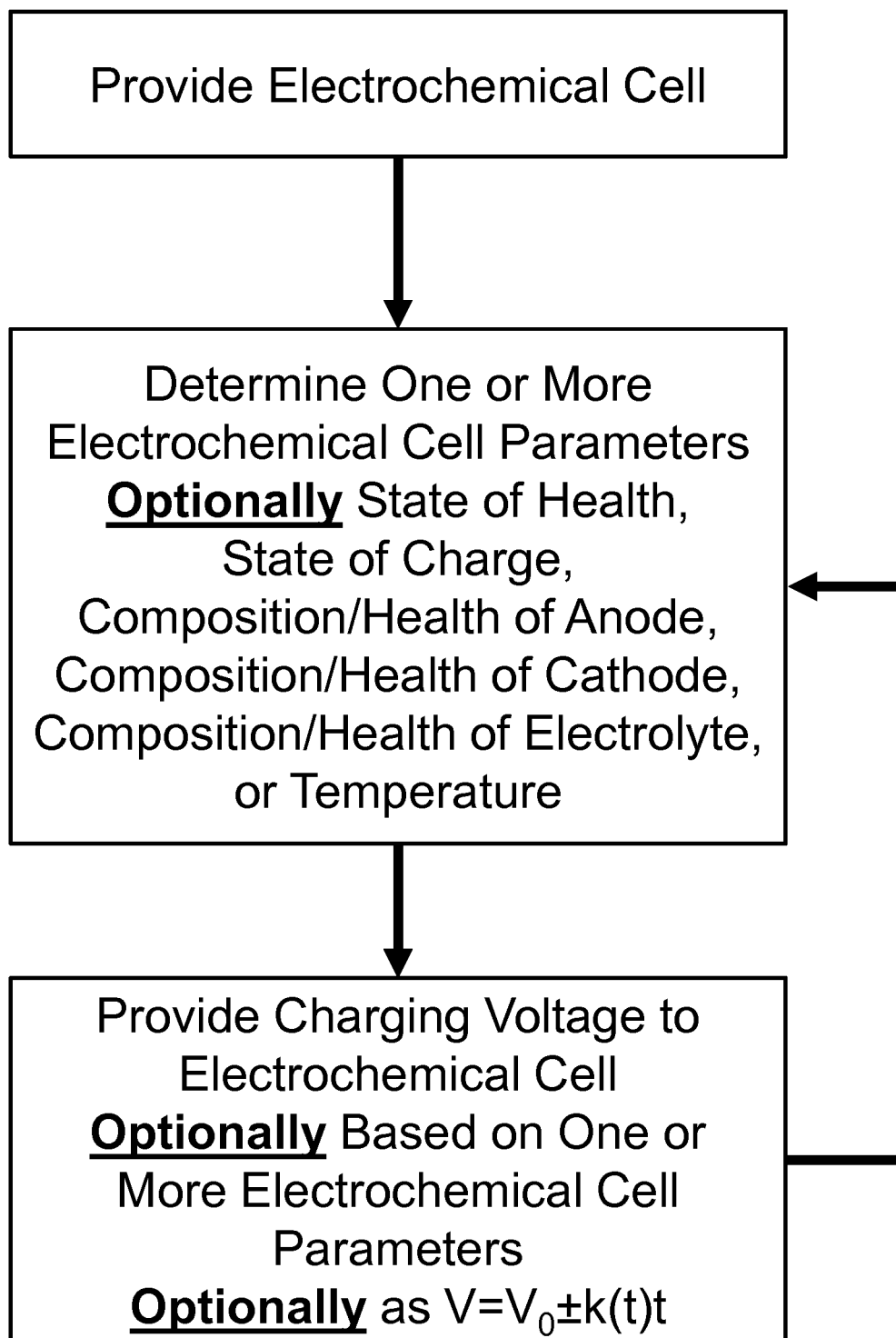


Figure 2

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## METHODS AND SYSTEMS FOR CHARGING ELECTROCHEMICAL CELLS

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application 61/376,208 filed Aug. 23, 2010, which is hereby incorporated by reference in its entirety.

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

### BACKGROUND OF INVENTION

Since their invention over 200 years ago, electrical batteries have become a global multibillion-dollar industry that demonstrates continued growth. Over the last few decades, revolutionary advances have been made in electrochemical storage and conversion devices expanding the capabilities of these systems in a variety of fields including portable electronic devices, transportation, air and space craft technologies, renewable energy technologies, and biomedical devices. Current state of the art electrochemical storage and conversion devices have designs and performance attributes that are specifically engineered to provide compatibility with a diverse range of application requirements and operating environments. For example, advanced electrochemical storage systems have been developed spanning the range from high energy density batteries exhibiting very low self-discharge rates and high discharge reliability for implanted medical devices to inexpensive, light weight rechargeable batteries providing long runtimes for a wide range of portable electronic devices, to high capacity batteries for military and aerospace applications capable of providing extremely high discharge rates over short time periods.

With the expansion and proliferation of personal electronic devices, electric automobiles, and other battery-powered technologies, development of lighter, more efficient, and more powerful battery technologies has been identified as essential for the continued development of these technologies. For example, continued development in the fields of electric vehicles and aerospace engineering has also created a need for mechanically robust, high reliability, high energy density and high power density batteries capable of good device performance in a useful range of operating environments. Furthermore, the demand for miniaturization in the field of consumer electronics and instrumentation continues to stimulate research into novel design and material strategies for reducing the sizes, masses and form factors of high performance batteries.

Batteries may be classified into two categories; disposable or 'primary' batteries, and rechargeable or 'secondary' batteries. Generally having higher energy densities than secondary batteries, primary batteries such as alkaline and zinc-carbon batteries are often used in portable electronic devices having low current drain. Secondary batteries such as nickel-cadmium, nickel-zinc, nickel metal hydride, and lithium-ion batteries are used in a wide range of applications such as power tools, medical equipment, personal portable electronic devices, and all-electric plug-in vehicles. Although secondary batteries have a higher initial cost than primary batteries, they may be charged very cheaply and used many times, thus having a lower total cost of use. Batteries from both categories consist of a positive electrode (cathode during discharge),

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a negative electrode (anode during discharge) and an electrolyte. The electrolyte contains ionic species that function as charge carriers for the oxidation and reduction processes occurring at the electrodes. During charge and discharge, electrodes exchange ions with electrolyte and electrons with an external circuit (a load or a charger).

Many recent advances in electrochemical storage and conversion technology are directly attributable to discovery and integration of new materials for battery components. Lithium battery technology, for example, continues to rapidly develop, at least in part, due to the discovery of novel electrode and electrolyte materials for these systems. Development of intercalation host materials for negative electrodes has led to the discovery and commercial implementation of lithium ion based secondary batteries exhibiting high capacity, good stability and useful cycle life. As a result of these advances, lithium based battery technology is currently widely adopted for use in a range of important applications including primary and secondary electrochemical cells for portable electronic systems.

The element lithium has a unique combination of properties that make it attractive for use in an electrochemical cell. First, it is the lightest metal in the periodic table having an atomic mass of 6.94 AMU. Second, lithium has a very low electrochemical oxidation/reduction potential, i.e.,  $-3.045$  V vs. NHE (normal hydrogen reference electrode). This unique combination of properties enables lithium based electrochemical cells to have very high specific capacities. Advances in materials strategies and electrochemical cell designs for lithium battery technology have realized electrochemical cells capable of providing useful device performance including: (i) high cell voltages (e.g. up to about 3.8 V), (ii) substantially constant (e.g., flat) discharge profiles, (iii) long shelf-life (e.g., up to 10 years), and (iv) compatibility with a range of operating temperatures (e.g.,  $-20$  to  $60$  degrees Celsius). As a result of these beneficial characteristics, primary lithium batteries are widely used as power sources in a range of portable electronic devices and in other important device applications including, electronics, information technology, communication, biomedical engineering, sensing, military, and lighting.

State of the art lithium ion secondary batteries provide excellent charge-discharge characteristics, and thus, have been widely adopted as power sources in portable electronic devices, such as cellular telephones and portable computers. U.S. Pat. Nos. 6,852,446, 6,306,540, 6,489,055, and "Lithium Batteries Science and Technology" edited by Gholam-Abbas Nazri and Gianfranco Pistoia, Kluwer Academic Publishers, 2004, are directed to lithium and lithium ion battery systems which are hereby incorporated by reference in their entireties.

Charging a secondary battery typically involves passing direct current (d.c.) electricity through the battery in a manner to reverse the discharge process. During charging, electrochemical oxidation of the active material occurs at the positive electrode, while electrochemical reduction takes place at the negative electrode. The charging conditions (e.g., charging voltage, charging current, temperature, overvoltage, etc.) play a significant role in establishing and maintaining the useful lifetime of a battery system. In addition, if current continues to be provided after completion of recharging, the battery may be provided in an overcharge state, which can result in degradation of battery components, for example, via decomposition of electrolyte.

Lithium ion batteries, for example, are commonly charged using the constant-current, constant voltage (CCCV) method. In the CCCV method, the current is held constant typically



until the battery voltage reaches a pre-defined value, for example, the voltage in which gassing is likely to begin. At this point, the voltage is held constant while the current is allowed to decline exponentially. In some charging systems, a top-off charge also is provided periodically for certain recharge cycles. In addition to controlling applied constant current and final voltage, charging systems for lithium ion batteries typically monitor and control some battery safety parameters such as temperature and overcharge currents and voltages. In addition, some chargers for these batteries also take into account the battery cycle life to adjust the CCCV conditions. Occasionally, linear voltammetry (LV) is used in systems and methods to charge batteries, such as lithium ion batteries, wherein a charging voltage is applied that varies linearly with time over a minimum and maximum voltage range.

Many state of the art CCCV and LV procedures and systems for charging lithium ion batteries, however, fail to take into account certain system parameters that can significantly impact cycling performance and battery lifetime. These parameters include, for example, the battery 'state of health' (SOH), and/or the health and/or composition of specific system components such as the anode, cathode, and electrolyte (See, e.g., US 2010/0090650). The SOH varies with the system 'history', such as for the most common charge/discharge cycles, overcharge and over-discharge, and thermal aging. In some instances, for example, degradation of one of the active components: anode, cathode and electrolyte, affects the cell's SOH. The failure of state of the art charging systems to take into account the SOH, for example, may result in premature battery aging and irreversible losses in stored energy upon cycling.

As will be clear from the foregoing, there exists a need in the art for an improved methods and systems for charging batteries. Specifically, chargers and charging methods are needed that take into account system parameters that can affect cycling performance and battery lifetime, such as the battery's SOH and the health and/or composition of system components.

#### SUMMARY OF THE INVENTION

The invention provides systems and methods for charging an electrochemical device, such as a secondary electrochemical cell. Charging systems and methods of some embodiments provide charging parameters, such as charging voltage and charging current, that vary in a preselected manner as a function of time so as to enhance the overall device performance (e.g., specific capacity, discharge rate, etc.) cycling properties and useful lifetime of a secondary electrochemical cell. Charging systems and methods of some embodiments provide charging parameters, such as time varying charging voltages and charging currents, that take into consideration important electrochemical cell properties that impact device performance, cycling and lifetime, such as the state of health of an electrochemical cell, state of charge of the electrochemical cell, and/or the health and/or composition of specific system components such as the anode, cathode, and electrolyte and/or the cycle history of the electrochemical cell (e.g., cycle number, etc.).

In an aspect, the invention provides a method of charging an electrochemical cell, the method comprising the steps of: (1) providing the electrochemical cell, for example in a partially or completely discharged state; and (2) providing a time varying charging voltage to the electrochemical cell, thereby generating a charging current resulting in charging of the electrochemical cell; wherein the time varying charging volt-

age has a non-linear time dependency provided by  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ;  $V$  is the time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage,  $k(t)$  is a time dependent voltage rate, wherein  $V_{min}$  is a minimum voltage provided to the electrochemical cell and  $V_{max}$  is a maximum voltage provided to the electrochemical cell. In an embodiment, the invention provides a nonlinear voltammetry method for charging an electrochemical cell.

In an embodiment,  $k(t)$  is not a linear function with respect to time, for example, wherein  $k(t)$  is a quadratic, polynomial, or exponential function with respect to time or any combination of these. In an embodiment,  $k(t)$  is the rate of voltage change in units of V/s. In an embodiment,  $k(t)$  defines a charging voltage as a function of time that is different from that provided in a constant-current constant-voltage method. In an embodiment,  $k(t)$  defines a charging voltage as a function of time that is different from that provided in a linear voltammetry charging method. As used herein, the expression "time varying" refers to a charging voltage that changes as a function of time over the charging process, for example, changing in a pre-selected manner so as to optimize the overall performance, cycling properties and/or lifetime of the electrochemical cell. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell reverses the discharge process by providing current to the electrochemical cell, thereby resulting in complete or partial charging of the electrochemical cell. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell results in electrochemical oxidation at the positive electrode of the electrochemical cell and results in electrochemical reduction at the negative electrode of the electrochemical cell, thereby resulting in complete or partial charging of the electrochemical cell. In an embodiment, for example, the charging voltage is provided to the electrochemical cell over a charging time selected from the range of 1 minute to 100 hours, thereby resulting in complete or partial charging of the electrochemical cell.

In an embodiment, the method of the invention further comprises the step of determining the state of health of the electrochemical cell, state of charge of the electrochemical cell, the composition of the positive electrode of the electrochemical cell, the composition of the negative electrode of the electrochemical cell, the composition of the electrolyte of the electrochemical cell or any combination of these; wherein the non-linear time dependency is derived, at least in part, from the state of health of the electrochemical cell, state of charge of the electrochemical cell, the composition of the positive electrode, the composition of the negative electrode, the composition of the electrolyte or any combination of these. In this aspect of the invention, the dependence of the charge voltage as a function of time is pre-selected based on one or more parameters derived from the electrochemical cell such as the state of health of the electrochemical cell, state of charge of the electrochemical cell, the composition of the positive electrode, the composition of the negative electrode, the composition of the electrolyte or any combination of these. For example, the invention includes methods and systems wherein  $k(t)$  is also a function of the electrochemical cell such as the state of health of the electrochemical cell, state of charge of the electrochemical cell, the composition of the positive electrode, the composition of the negative electrode, the composition of the electrolyte or any combination of these.

In an embodiment, the charging voltage has a rate of change that is not constant during at least a portion of the charging process and optionally for the entire duration of the charging process. In an embodiment, for example, the step of

providing a charging voltage to the electrochemical cell comprises providing a time varying charging current to the electrochemical cell, for example, a charging current having a non-linear time dependency for at least a portion of, and optionally all of, the charging process. In an embodiment, for example, the charging voltage has a rate of change having an inverse relationship with a rate of change of the charging current over at least a portion of, and optionally all of, the charging process. In an embodiment, for example, a product of the rate of change of the charging voltage and the rate of change of the charging current is constant for at least a portion of, and optionally all of, the charging process. In an embodiment, for example, the charging voltage has a rate of change having an inverse relationship with a rate of change of the charging current raised to an exponential factor for at least a portion of, and optionally all of, the charging process. In an embodiment of this aspect, for example, the method of the invention further comprises a step of selecting the exponential factor for which to determine the charging voltage as a function of time so as to partially or fully charge the electrochemical cell within a selected time, for example, a step of selecting an exponential factor that is greater than zero.

The parameters defining the time varying charging voltage and/or time varying charging current in the methods of the invention may be selected for a given electrochemical device, state of an electrochemical device or application for an electrochemical device. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell takes into account the state of health of the electrochemical cell. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell takes into account the health and/or composition of one or more components of the electrochemical cell, such as the anode, cathode and/or electrolyte. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell takes into account the cycling history, such as the number of previous charge and discharge cycles. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell takes into account the discharge and/or charge history, such as the discharge rates or charge rates for previous charge and discharge cycles. In an embodiment, for example, the time varying charging voltage provided to the electrochemical cell results in enhanced device performance, such as increased cycling performance and/or useful lifetime of the electrochemical cell.

In an embodiment, for example,  $k(t)$  is selected so as to provide charging voltages as a function of time selected to provide efficient charging for charging times ranging from 1 minute to 100 hours. In an embodiment, for example,  $k(t)$  is selected so as to provide charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods.

In an embodiment, for example, the expression  $k(t)$  is provided by Equation I:

$$k(t) = \frac{C}{r_i(t)^n}; \quad (\text{Equation I})$$

wherein  $C$  is a constant,  $r_i(t)$  is the time rate of current flowing into the electrochemical cell,  $t$  is time, and  $n$  is greater than 0. In an embodiment, for example,

$$r_i = \frac{\partial i(t)}{\partial t};$$

wherein  $i$  is the current flowing to the electrochemical cell and  $t$  is time. In an embodiment, for example,  $r_i(t)$  provides charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods. In an embodiment, for example,  $C$  has a value providing charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods. In an embodiment, for example,  $C$  has a value providing charging voltages as a function of time selected to provide efficient partial or complete charging for charging times ranging from 1 minute to 100 hours. In an embodiment, for example,  $n$  has a value providing charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods. In an embodiment, for example,  $n$  has a value providing charging voltages as a function of time selected to provide efficient partial or complete charging for charging times ranging from 1 minute to 100 hours. In an embodiment, for example,  $V_0$ ,  $V_{min}$  and  $V_{max}$  have values providing charging voltages as a function of time selected to provide efficient partial or complete charging for charging times ranging from 1 minute to 100 hours.

In another aspect, the invention provides a battery charging system comprising: (1) two or more electrodes for making an electrical connection to terminals of an electrochemical cell; (2) a power supply positioned in electrical communication with the two or more electrodes for providing a controllable time varying charging voltage to the two or more electrodes; and (3) a processor for controlling the charging voltage provided by the power supply, wherein the processor provides a time varying charging voltage to the electrochemical cell, thereby generating a charging current resulting in charging of the electrochemical cell; wherein the time varying charging voltage has a non-linear time dependency provided by  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ; wherein  $V$  is the time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage,  $k(t)$  is a time dependent voltage rate, wherein  $V_{min}$  is a minimum voltage and  $V_{max}$  is a maximum voltage. The system of this aspect may incorporate hardware (e.g. processor, etc.) and/or software components to implement any of the charging methods described herein, such as using any of the charging voltage and/or charging current parameters, expression or equations as set forth herein. In an embodiment, for example, the processor component includes hardware (e.g. processor, etc.) and/or software components that implements a charging method as described herein.

In an embodiment, for example, the processor controls the charging voltage such that the charging voltage has a rate of change that is not constant for at least a portion of, and optionally all of, the charging process. In an embodiment, for example, the power supply provides a controllable time varying charging current to the two or more electrodes. In an embodiment, for example, the processor controls the charging current such that the charging current has a rate of change that is not constant. In an embodiment, for example, the processor controls the charging voltage and the charging current such that the charging voltage has a rate of change having an inverse relationship with a rate of change of the charging

current, for at least a portion of, and optionally all of, the charging process. In an embodiment, for example, the processor controls the charging voltage and the charging current such that a product of a rate of change of the charging voltage and a rate of change of the charging current is constant, for at least a portion of, and optionally all of, the charging process. In an embodiment, for example, the processor controls the charging voltage and the charging current such that the charging voltage has a rate of change having an inverse relationship with a rate of change of the charging current raised to an exponential factor, such as an exponential factor greater than zero. In an embodiment of this aspect, for example, the processor controls the exponential factor so as to partially or completely charge the battery in a selected time.

In another aspect, the invention provides a secondary battery charging controller comprising: a control circuit for controlling a charging voltage provided by a power supply for charging a secondary battery, wherein the control circuit controls the charging voltage to provide a time varying charging voltage to the secondary battery; wherein the time varying charging voltage has a non-linear time dependency provided by  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ; wherein  $V$  is the time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage,  $k(t)$  is a time dependent voltage rate, wherein  $V_{min}$  is a minimum voltage and  $V_{max}$  is a maximum voltage. The charging controller of this aspect may incorporate hardware (e.g. processor, etc.) and/or software components to implement any of the charging methods described herein, such as using any of the charging voltage and/or charging current parameters, expression or equations as set forth herein.

The methods and devices of the present invention are useful for charging a range of electrochemical devices, such as electrochemical cells, useful for a range of applications including portable electronics, transportation, aerospace, renewable energy and biomedical applications. In an embodiment, for example, the electrochemical cell is a secondary battery. In an embodiment, for example, the electrochemical cell is a lithium ion battery, a Ni-cadmium battery, a lithium polymer battery, nickel metal hydride battery, or a lead-acid battery.

Without wishing to be bound by any particular theory, there can be discussion herein of beliefs or understandings of underlying principles or mechanisms relating to the invention. It is recognized that regardless of the ultimate correctness of any explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a battery charging system of the invention operably connected to a secondary electrochemical cell to provide partial or complete charging.

FIG. 2 provides an overview of a method of charging an electrochemical cell.

#### DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawings, like numerals indicate like elements and the same number appearing in more than one drawing refers to the same element. In addition, hereinafter, the following definitions apply:

The term "electrochemical cell" refers to devices and/or device components that convert chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells have two or more electrodes (e.g., positive and negative electrodes) and an electrolyte, wherein electrode reactions occurring at the electrode surfaces result in charge

transfer processes. Electrochemical cells include, but are not limited to, primary batteries, secondary batteries and electrolysis systems. General cell and/or battery construction is known in the art, see e.g., U.S. Pat. Nos. 6,489,055, 4,052, 539, 6,306,540, Seel and Dahn J. Electrochem. Soc. 147(3) 892-898 (2000).

The term "capacity" is a characteristic of an electrochemical cell that refers to the total amount of electrical charge an electrochemical cell, such as a battery, is able to hold. Capacity is typically expressed in units of ampere-hours. The term "specific capacity" refers to the capacity output of an electrochemical cell, such as a battery, per unit weight. Specific capacity is typically expressed in units of ampere-hours  $\text{kg}^{-1}$ .

The term "discharge rate" refers to the current at which an electrochemical cell is discharged. Discharge current can be expressed in units of ampere-hours. Alternatively, discharge current can be normalized to the rated capacity of the electrochemical cell, and expressed as  $C/(X \text{ t})$ , wherein  $C$  is the capacity of the electrochemical cell,  $X$  is a variable and  $t$  is a specified unit of time, as used herein, equal to 1 hour.

Electrode refers to an electrical conductor where ions and electrons are exchanged with electrolyte and an outer circuit. "Positive electrode" and "cathode" are used synonymously in the present description and refer to the electrode having the higher electrode potential in an electrochemical cell (i.e. higher than the negative electrode). "Negative electrode" and "anode" are used synonymously in the present description and refer to the electrode having the lower electrode potential in an electrochemical cell (i.e. lower than the positive electrode). Cathodic reduction refers to a gain of electron(s) of a chemical species, and anodic oxidation refers to the loss of electron(s) of a chemical species. Positive electrodes and negative electrodes of the present electrochemical cell may further comprises a conductive diluent, such as acetylene black, carbon black, powdered graphite, coke, carbon fiber, and metallic powder, and/or may further comprises a binder, such polymer binder. Useful binders for positive electrodes in some embodiments comprise a fluoropolymer such as polyvinylidene fluoride (PVDF). Positive and negative electrodes of the present invention may be provided in a range of useful configurations and form factors as known in the art of electrochemistry and battery science, including thin electrode designs, such as thin film electrode configurations. Electrodes are manufactured as disclosed herein and as known in the art, including as disclosed in, for example, U.S. Pat. Nos. 4,052, 539, 6,306,540, 6,852,446. For some embodiments, the electrode is typically fabricated by depositing a slurry of the electrode material, an electrically conductive inert material, the binder, and a liquid carrier on the electrode current collector, and then evaporating the carrier to leave a coherent mass in electrical contact with the current collector.

"Electrode potential" refers to a voltage, usually measured against a reference electrode, due to the presence within or in contact with the electrode of chemical species at different oxidation (valence) states.

"Electrolyte" refers to an ionic conductor which can be in the solid state, the liquid state (most common) or more rarely a gas (e.g., plasma).

"Charging voltage" refers to a voltage applied to an electrochemical device, such as a secondary electrochemical cell, to charge the electrochemical device.

"Charging current" refers to a current applied to an electrochemical device, such as a secondary electrochemical cell, to charge the electrochemical device.

FIG. 1 illustrates a battery charging system of the invention operably connected to a secondary electrochemical cell to provide partial or complete charging. Battery charging sys-

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tem 100 comprises electrodes 101 and 102 positioned in electrical communication with power supply 103 and, optionally processor 104. Electrodes 101 and 102 are positioned to make electrical connections with terminals 105 and 106 of the secondary electrochemical cell 107, such as a lithium ion battery. Power supply 103 is a controllable power supply and receives one or more control signals 108 from processor 104 for controlling a time varying charging voltage provided between electrodes 101 and 102. The charging voltage provided by power supply 103 generates a charging current capable of partially or fully charging secondary electrochemical cell 107, optionally over a preselected charging time. Processor 104 controls a charging voltage provided by power supply 103 to electrochemical cell as a function of time. In a specific embodiment, for example, Processor 104 controls a charging voltage provided by power supply 103 to electrochemical cell according to  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ; wherein  $V$  is a time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage and  $k(t)$  is a time dependent voltage rate wherein  $V_{min}$  is a minimum voltage and  $V_{max}$  is a maximum voltage. Optionally,  $k(t)$  is a function of a charging current provided by power supply 103 to electrochemical cell 107.

Optionally, processor 104 also monitors, measures or otherwise receives an input of one or more parameters relating to secondary electrochemical cell 107 over one or more monitoring connections 109 operably connected secondary electrochemical cell 107. In an embodiment, for example, processor 104 determines, or is provided an input, one or more parameters corresponding to the electrochemical cell, such as the state of health, state of charge, cycle history, composition and/or health of anode, composition and/or health of cathode, composition and/or health of the electrolyte or cell temperature of secondary electrochemical cell 107. Optionally, processor 104 controls a charging voltage provided by power supply 103 to electrochemical cell 107 based on one or more parameters of electrochemical cell 107. Optionally, processor 104 measures a charging voltage provided to electrochemical cell 107. Optionally, processor 104 measures a charging current provided to electrochemical cell 107. Optionally, processor 104 controls a charging voltage provided by power supply 103 to electrochemical cell 107 based on a charging current provided to electrochemical cell 107. Optionally, processor 104 controls a charging voltage provided by power supply 103 to electrochemical cell 107 based on the total charge provided to electrochemical cell 107 by power supply 103.

FIG. 2 provides an overview of a method of charging an electrochemical cell of the invention. Initially, an electrochemical cell is provided, for example an electrochemical cell in a partially or completely discharged state: Next, one or more parameters of the electrochemical cell are determined, such as state of health, state of charge, composition and/or health of the anode, composition and/or health of the cathode, composition and/or health of the electrolyte, cycling history or cell temperature. Next, a charging voltage is provided to the electrochemical cell, thereby generating thereby generating a charging current resulting in charging of said electrochemical cell, for example a time varying charging current. Optionally, the charging voltage provided to the electrochemical cell as a function of time is based on one or more of the parameters of the electrochemical cell, for example as determined by, or provided as input to, a charging controller or processor. Optionally, the charging voltage provided to the electrochemical cell is based on a charging current provided to the electrochemical cell. Optionally, the charging voltage provided to the electrochemical cell is based on the total charge provided to the electrochemical cell or the initial dis-

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charged state of the electrochemical cell. Optionally, the step of determining the one or more parameters of the electrochemical cell is repeated and the charging voltage provided to the electrochemical cell is controlled based on one or more of the newly determined parameters.

#### EXAMPLE 1

##### Battery Charging System

Lithium ion batteries are commonly charged using the constant-current, constant-voltage (CCCV) method. In this method, for example, the battery charger controls applied constant current and final voltage, optionally together with some battery safety parameters such as temperature and over-charge currents and voltages. In addition, some chargers or methods may take into account the battery cycle life to adjust the CCCV conditions. Occasionally linear voltammetry (LV) is applied to charge and discharge batteries. In such technique, applied voltage  $V$  varies linearly with time:

$$V = V_0 \pm kt, \text{ and } V_{min} \leq V \leq V_{max};$$

wherein  $V_0$ =starting voltage,  $t$  is time,  $k$ =constant and  $V_{min}$ =minimum voltage,  $V_{max}$ =maximum voltage.

The conventional CCCV procedure, however, does not take into account the battery state of health (SOH) resulting in premature battery aging and irreversible losses in stored energy upon cycling. Using cycle life as metrics to change the CCCV parameters helps gain in cycle life but only to a limited extent. In addition, CCCV is not a "natural way" to charge batteries because of the nonlinearity of the current response to a voltage change.

The present invention provides systems and methods to charge batteries in a different way than CCCV and LV that take into account the battery current response to changes in the applied voltage. In an embodiment, for example, non-linear voltammetry (NLV) is used for charging, where the rate of voltage change ( $k$  in V/s) is not a constant and varies with time. For some applications, NLV can be described in terms of the equation:  $V = V_0 \pm k(t)t$ ,  $V_{min} \leq V \leq V_{max}$ , wherein,  $t$  is time,  $V_0$  is a starting voltage,  $k(t)$  is a time dependent voltage rate (V/s),  $V_{min}$  is a minimum voltage, and  $V_{max}$  is a maximum voltage.

In some embodiments, the invention provides a NLV battery charging method; wherein the time dependent voltage rate  $k(t)$  is fixed according to different criteria such as The time rate " $r_i$ " of current flowing in the cell,  $i(A)$  as defined by the equation:

$$r_i = \frac{\partial i(t)}{\partial t};$$

and

The relationship between  $k(t)$  and  $r_i$  is:

$$k(t) \times r_i^n = \text{constant};$$

where  $n$  is an adjustable parameter and wherein  $n > 0$ .

This equation fixes the voltage rate  $k(t)$  to the current rate  $r_i$  so as  $k(t)$  and  $r_i$  vary in opposite ways, i.e.  $k(t)$  increases when  $r_i$  decreases. In this equation, parameter  $n$  is adjusted to allow for a full battery charge in a preselected time according to the user.

The methods of the invention may be implemented via software or hardware (e.g., processor, etc.) embodiments. In some embodiments, the charging parameters (e.g. charging voltage, charging current, etc.) are adjusted to meet certain

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the battery charge criteria: battery type, cycle history, total charging time; voltage limits; current limits; enhance charge capacity and cycle life.

#### STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

All references throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the present invention and it will be apparent to one skilled in the art that the present invention may be carried out using a large number of variations of the devices, device components, methods steps set forth in the present description. As will be obvious to one of skill in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including any isomers, enantiomers, and diastereomers of the group members, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure.

Whenever a range is given in the specification, for example, a voltage range, a current range, a temperature range, a time range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranged given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when composition of matter are claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds

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for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

One of ordinary skill in the art will appreciate that starting materials, biological materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, and biological methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

I claim:

1. A method of charging an electrochemical cell, the method comprising the steps of:

providing the electrochemical cell; and

providing a time varying charging voltage to said electrochemical cell, thereby generating a charging current resulting in charging of said electrochemical cell; wherein said time varying charging voltage has a non-linear time dependency provided by  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ; wherein  $V$  is the time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage,  $k(t)$  is a time dependent voltage rate,  $V_{min}$  is a minimum voltage and  $V_{max}$  is a maximum voltage.

2. The method of claim 1, further comprising the step of determining the state of health of the electrochemical cell, the state of charge of the electrochemical cell, the composition of the positive electrode of the electrochemical cell, the composition of the negative electrode of the electrochemical cell, the composition of the electrolyte of the electrochemical cell or any combination of these; wherein said non-linear time dependency is derived, at least in part, from said state of health of the electrochemical cell, said state of charge of the electrochemical cell, said composition of the positive electrode, said composition of the negative electrode, said composition of the electrolyte or any combination of these.

3. The method of claim 1, wherein said charging voltage has a rate of change that is not constant.

4. The method of claim 1, wherein said charging current has a non-linear time dependency.

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5. The method of claim 1, wherein said charging voltage has a rate of change having an inverse relationship with a rate of change of said charging current.

6. The method of claim 5, wherein a product of said rate of change of said charging voltage and said rate of change of said charging current is constant.

7. The method of claim 1, wherein said charging voltage has a rate of change having an inverse relationship with a rate of change of said charging current raised to an exponential factor.

8. The method of claim 7, wherein said exponential factor is greater than zero.

9. The method of claim 7, further comprising a step of selecting said exponential factor to charge said electrochemical cell in a selected time.

10. The method of claim 1, wherein  $k(t)$  provides charging voltages as a function of time selected to provide efficient charging for charging times ranging from 1 minute to 100 hours.

11. The method of claim 1, wherein  $k(t)$  provides charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods.

12. The method of claim 11, wherein  $k(t)$  is provided by the expression:

$$k(t) = \frac{C}{r_i(t)^n};$$

wherein  $C$  is a constant,  $r_i(t)$  is the time rate of current flowing into the electrochemical cell,  $t$  is time and  $n$  is greater than 0.

13. The method of claim 12, wherein  $C$  has a value providing charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods.

14. The method of claim 12, wherein  $C$  has a value providing charging voltages as a function of time selected to provide efficient charging for charging times ranging from 1 minute to 100 hours.

15. The method of claim 12, wherein  $r_i(t)$  provides charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods.

16. The method of claim 12, wherein  $n$  has a value providing charging voltages having a time dependence different from constant-current, constant voltage charging methods, constant current charging methods, constant voltage charging methods and linear voltammetry charging methods.

17. The method of claim 12, wherein  $n$  has a value providing charging voltages as a function of time selected to provide efficient charging for charging times ranging from 1 minute to 100 hours.

18. The method of claim 1, wherein  $V_0$ ,  $V_{min}$  and  $V_{max}$  have values providing charging voltages as a function of time selected to provide efficient charging for charging times ranging from 1 minute to 100 hours.

19. The method of claim 1, wherein said charging voltage is provided to said electrochemical cell over a charging time selected from the range of 1 minute to 100 hours.

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20. The method of claim 1, wherein said electrochemical cell is a secondary battery.

21. The method of claim 1, wherein said electrochemical cell is a lithium ion battery, a Ni-cadmium battery, a lithium polymer battery, nickel metal hydride battery, or a lead-acid battery.

22. A battery charging system comprising:

two or more electrodes for making an electrical connection to terminals of an electrochemical cell;

a power supply positioned in electrical communication with said two or more electrodes for providing a controllable time varying charging voltage to said two or more electrodes; and

a processor for controlling said charging voltage provided by the power supply, wherein said processor provides a time varying charging voltage to said electrochemical cell, thereby generating a charging current resulting in charging of said electrochemical cell; wherein said time varying charging voltage has a non-linear time dependency provided by  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ; wherein  $V$  is the time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage,  $k(t)$  is a time dependent voltage rate,  $V_{min}$  is a minimum voltage and  $V_{max}$  is a maximum voltage.

23. The system of claim 22, wherein said processor controls said charging voltage such that said charging voltage has a rate of change that is not constant.

24. The system of claim 22, wherein said power supply provides a controllable time varying charging current to said two or more electrodes.

25. The system of claim 22, wherein said processor controls said charging current such that said charging current has a rate of change that is not constant.

26. The system of claim 22, wherein said processor controls said charging voltage and said charging current such that said charging voltage has a rate of change having an inverse relationship with a rate of change of said charging current.

27. The system of claim 22, wherein said processor controls said charging voltage and said charging current such that a product of a rate of change of said charging voltage and a rate of change of said charging current is constant.

28. The system of claim 22, wherein said processor controls said charging voltage and said charging current such that said charging voltage has a rate of change having an inverse relationship with a rate of change of said charging current raised to an exponential factor.

29. The system of claim 28, wherein said exponential factor is greater than zero.

30. The system of claim 28, wherein said processor controls said exponential factor so as to charge said battery in a selected time.

31. A secondary battery charging controller comprising:

a control circuit for controlling a charging voltage provided by a power supply for charging a secondary battery, wherein said control circuit controls said charging voltage to provide a time varying charging voltage to said electrochemical cell, thereby generating a charging current resulting in charging of said electrochemical cell; wherein said time varying charging voltage has a non-linear time dependency provided by  $V = V_0 \pm k(t)t$  and  $V_{min} \leq V \leq V_{max}$ ; wherein  $V$  is the time varying charging voltage,  $t$  is time,  $V_0$  is an initial voltage,  $k(t)$  is a time dependent voltage rate,  $V_{min}$  is a minimum voltage and  $V_{max}$  is a maximum voltage.

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